

FLUX REACTIONS IN BRAZING OF STAINLESS STEEL

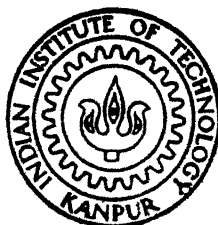
by

ATUL KUMAR SRIVASTAVA

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DEPARTMENT OF METALLURGICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY KANPUR

MARCH, 1992

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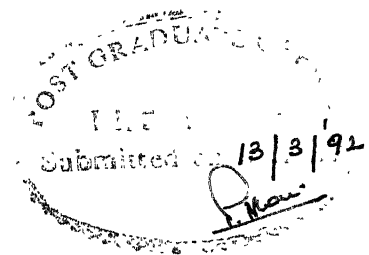
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FLUX REACTIONS IN BRAZING OF STAINLESS STEEL

*A Thesis Submitted
In Partial Fulfilment of the Requirements
for the Degree of*
MASTER OF TECHNOLOGY

by
ATUL KUMAR SRIVASTAVA

to the
**DEPARTMENT OF METALLURGICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY KANPUR**
MARCH, 1992



CERTIFICATE

It is certified that the work contained in the thesis entitled "Flux Reactions in Brazing of Stainless Steel " by Atul kumar srivastava, has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

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ABSTRACT

Laboratory studies have been carried out in the present work to study the flux-metal reactions in the temperature range of 600-1100°C. Both commercial and synthetic fluxes consisting of borax, boric acid and potassium chloride were used for the study. Experiments involved finding changes in weight of the metal strips when in contact with the flux and areas of spread of silver-copper-tin alloys on the stainless steel plate. A few experiments on dip coatings and electrochemical nature of reactions were also carried out. The bands appearing on the peripheries of spread mass as well as the coating were analyzed for various elements using SEM.

Results show that commercial flux causes blackening of the stainless steel plate in about 5-10 minutes when the flux is placed on the plate but not when the plate is dipped in the flux. Flux vapours accelerate the corrosion attack on the parts which are not dipped in the flux. Flux promotes wetting when filler metal is added immediately after melting the flux otherwise poor wetting occurs. Reoxidation of chromium in the plate is believed to be responsible for blackening as well as non-wetting of the plate. The synthetic fluxes do not result in blackening of the substrate. Binary mixtures of borax and boric acid do not yield

wetting but addition of 10-20 % of potassium chloride produce good wetting. Best results are obtained with 90 % boric acid, 10 % potassium chloride flux and pure copper as filler alloy. All the alloys of silver and copper also wet well the stainless steel substrate using the flux. Presence of potassium chloride in the flux causes silver and copper in the filler metal to go into the flux as ions and get deposited in the substrate ahead of the droplet to give rise to bands. Coating of copper on stainless steel occurs when the strip is added in the flux without making contact with the liquid copper metal below. Similar deposition of silver brightens the surface of stainless steel and copper. Due to complex reactions occurring in the system it has not been feasible to correlate the electrochemical cell measurements with the theoretical analyses.

CHAPTER ONE

INTRODUCTION

1.1 Brazing

Brazing is a high temperature joining process as it is carried out at a temperature greater than 450°C but less than the melting point of base metal. It may thus be classified as a liquid-solid phase bonding process. The bond between the base metal and liquid filler metal is a metallurgical bond because no melting or large scale alloying of the base metal occurs. If done correctly the bond may result in a joint having strength four or five times the tensile strength of the filler metal itself¹.

In brazing, the parts being joined must be fitted by capillary action for which the joint spacing is kept small, approximately .006mm. If the filler metal is used to fill the joint by gravity rather than by capillary flow the process is called braze welding. The basic principle involved in wetting and capillary flow are given in the Appendix A.

Getting heat to the joint can be accomplished in many ways and the processes as categorized by the method of heating are as follows:

- (i) Torch brazing
- (ii) Furnace brazing
- (iii) Induction brazing
- (iv) Dip brazing
- (v) Resistance brazing

(vi) Infrared brazing

Important Advantages of the Brazing Process may be summarized as follows:

- (i) Economical fabrication of complex and multicomponent assemblies.
- (ii) Simple means for achieving extensive joint area or joint length.
- (iii) Joint temperature capability approaching that of base metal.
- (iv) Excellent stress distribution and heat transfer.
- (v) Ability to join cast materials to wrought metals and nonmetals to metals.
- (vi) Ability to join widely different metal thicknesses and to join dissimilar metals.
- (vii) Porous metal components, fiber and dispersion-strengthened composites can be joined.
- (viii) Ability to preserve protective metal coating or cladding.

Specific examples of only a few of the most important categories include: Automotive and aircraft applications, Aircraft structures, Engines and engine components, Electron tubes, vacuum equipment and nuclear components, Electronic components, probes and thermionic devices, Space-vehicle assemblies, and Miscellaneous applications.

1.2 Brazeability of Stainless Steels²

As a class, stainless steels are more difficult to braze than the carbon and low alloy steels. The difficulty is associated with the chromium content of stainless steels, which accounts for the presence of chromium oxide films on the surface of all stainless steels. These oxides which are refractory and strongly adherent, prevent wetting of the base metal by the molten filler metal. The types of stainless steels used are given in the Appendix B.

The adverse effect of oxides on wetting can be alleviated in any of four ways:

- (i) The steel can be chemically cleaned of surface oxide at room temperature, and shortly thereafter be heated to the brazing temperature in a chemically inert gaseous atmosphere.
- (ii) The steel, after less intensive cleaning, can be heated directly to the brazing temperature in a strongly reducing atmosphere, such as dry H_2 , which will chemically reduce the oxide.
- (iii) Heating and Brazing of clean substrate can be done in a vacuum.
- (iv) Active fluxes are used to dissolve the oxide film and to protect the joint from further oxidation during heating to brazing temperature.

1.3 Scope of the present studies

It may be noted that behavior of fluxes is important to study as they help in cleaning the surface of the work-piece to ensure wetting of the base metal by the filler metal and are simple to apply. Some flux may keep the work-piece clean by shielding it from oxidation while some by dissolving the oxides which are formed on the surface due to the reaction between the work and diffused oxygen through the flux. In some instances, however, complex reactions may occur which lead to the formation of surface films; for instance, on chromium-bearing workpiece, a black film is formed, which is presumed to be Iron fluoride³.

Different aspects of brazing, e.g. wetting, cleaning, use of fluxes, are given in the next chapter of literature review.

Exhaustive studies have been reported on flux reactions in soldering⁴⁻⁸ but not much literature is available on flux reactions in brazing. In the present work, experiments have been carried out to study the stability, cleaning behavior of fluxes and its effect on wetting of the stainless steel by different filler metals. The plan of work, details of experiments carried out, results obtained and discussion are given in the following chapters.

CHAPTER TWO

LITERATURE REVIEW

2.1 Brazing filler metals

Brazing filler metals have been classified by the American Welding Society into eight groups i.e. aluminium-silicon, copper-phosphorous, silver, gold, copper and copper-zinc, magnesium, nickel, and cobalt besides some unclassified filler metals for vacuum service purposes and reactive metals. Some of the points which may be important while selecting the braze filler metal for a particular application are discussed below⁹:

- (i) Melting point of the braze filler metal must be less than that of base metal and any successive joint should use the filler metal having melting point less than the melting point of previously used braze filler metal.
- (ii) Liquation phenomenon occurs with braze filler metal having large melting range. The liquid alloy when cooled below its liquidus temperature separates out into solid and liquid phases having different compositions. If cooled slowly liquid tends to flow ahead along the joint, leaving behind a solid skull of higher melting point. Such alloy must be rapidly heated and cooled.
- (iii) Phosphorous in Copper-Phosphorous filler metals acts as deoxidiser, and the filler metal acts as self fluxing on Copper metal. Fluxes are however needed while brazing

filler metals should never be used in brazing of ferrous and nickle-based metals to avoid problems of Phosphorous embrittlement of such materials. Good fluidity of Copper-Phosphorous braze filler metals fill the joint easily.

- (iv) For general purpose, Copper, Copper-Zinc and silver groups of filler metals are widely used in brazing of Copper, Nickle, mild steel, cast iron and stainless steel materials. A base metal-filler metal combinations chart is shown in Table 2.1 .
- (v) Braze filler metals as well as base metals must be free of volatile metals such as Zinc, Cadmium, Palladium etc., if the brazed parts are to be used at high temperatures in vacuum.
- (vi) For brazing of cast iron it is important to have a surface free of graphite, sand and silicon oxide by appropriate cleaning method involving passing direct current between work and the tank containing molten salt at around 500°C . Other methods of cleaning involves grit blasting, chemical cleaning, oxidising flame etc.

A wide variety of filler metals is commercially available for brazing of stainless steel parts. Filler metals suitable for service at temperatures upto about 427°C are the BCu types. For temperatures upto 371°C the BAg types find extensive use. Filler metal suitable from (427 to 538°C) are the Cu-Mn-Ni type. Above

Table 2.1 Base metal-filler metal combinations

	Cu & Cu alloys	Carbon & low alloy steels	Cast iron	Stainless steels	Ni & Ni alloys
Cu & Cu alloys	B _{Ag} , B _{Au} , B _{CuP} , R _B CuZn				
Carbon & low alloy steels	B _{Ag} , B _{Au} , R _B CuZn	B _{Ag} , B _{Au} , B _{Cu} , B _{Ni} , R _B CuZn			
Cast iron	B _{Ag} , B _{Au} , R _B CuZn	B _{Ag} , R _B CuZn	B _{Ag} , B _{Ni} , R _B CuZn		
Stainless steels	B _{Ag} , B _{Au}	B _{Ag} , B _{Au} , B _{Cu} , B _{Ni}	B _{Ag} , B _{Au} , B _{Cu} , B _{Ni}	B _{Ag} , B _{Au} , B _{Cu} , B _{Ni}	
Ni & Ni alloys	B _{Ag} , B _{Au} , R _B CuZn	B _{Ag} , B _{Au} , B _{Cu} , B _{Ni} , R _B CuZn	B _{Ag} , B _{Cu} , R _B CuZn	B _{Ag} , B _{Au} , B _{Cu} , B _{Ni}	B _{Ag} , B _{Au} , B _{Cu} , B _{Ni}

B_{Ag} Silver group filler metals

B_{Au} Gold group filler metals

B_{Ni} Nickel group filler metals

B_{CuP} Copper-phosphorous group filler metals

B_{Cu} Copper group filler metals

R_BCuZn Copper-Zinc group filler metals

838°C, BNi filler metals or certain types containing the precious metals gold or Palladium are used⁹. Composition of BAg, BCu and BNi types filler metals at the melting process are shown in Table 2.2.

Studies have been carried out from time to time to minimize the requirements for scarce mineral commodities through conservation and substitution. Miller and Schwaneke¹⁰ has carried out studies on the interfacial characteristics of Ag filler metals on Copper, brass and steel base metals and based on information obtained they concluded that several properties are important to the development of silverless filler metal. A substitute filler metal should contain elements that are mutually soluble or form interfacial compounds with the Copper, brass, and steel base metals to promote good wetting and bond strength. The interface reactions should be time and temperature dependent to allow control of compound formed because it is usually brittle.

Cu-Mn-Sn alloys as brazing filler metals in order to reduce or eliminate the content of silver and toxic Cadmium have been developed by Chatterjee, Mingxi & Chilton¹¹. These alloys have the potential to join mild steel to mild steel at brazing temperature at or above 800°C, and to join Copper to mild steel at about 750°C. The developed alloys are Cu-11Mn-16Sn-INi, Cu-12Mn-19Sn, Cu-13Mn-20Sn-1Ci and Cu-10Mn-30Sn.

The demand for B free low melting, Ni based filler metals led to the development of three high temperature brazing alloys with low P and Fe which are 20.3Cr-11.5Si-0.5P-Bal.Ni,

SILVER GROUP

WS Classi- fication	X X X	Ag ± 1 %	X X X	Cu ± 1 %	X X X	Zn ± 2 %	X X X	Cd ± 1 %	X X X	Others %	X X X	Solidus C	X X X	Liquidus C
Ag 1		45		15		16		24		-		607		618
Ag 1a		50		15.5		16.5		18		-		627		635
Ag 2		35		26		21		18		-		607		702
Ag 2a		30		27		23		20		-		607		710
Ag 3		50		15.5		15.1		16		3 Ni		632		688
Ag 4		40		30		28		-		2 Ni		671		779
Ag 5		45		30		25		-		-		677		743
Ag 6		50		34		16		-		-		688		774
Ag 7		56		22		17		-		5 Sn		618		652
Ag 8		72		Bal		-		-		-		779		779
Ag 8a		72		"		-		-		.25-.5 Li		766		766
Ag 13		54		"		5		-		1 Ni		718		857
Ag 13a		56		"		-		-		2 Ni		771		893
Ag 18		60		"		-		-		10 Sn .025 P		602		718
Ag 19		92.5		"		-		-		.15-.3 Li		779		891
Ag 20		30		38		32		-		-		677		766
Ag 21		63		28.5		-		-		6 Sn 2.5 Ni		691		802

Note : 1 : Concentration of other elements is less than 0.15%
 2 : Sn and Ni Values are ± 0.5%

Table 2.2(a) Compositions of BAg filler metals

NICKEL GROUP

	X Cr X	X B X	X Si X	X Fe X	X P/C X	Solidus X	Liquidus X
	+1 %	%	%	%	%	%	C
Ni 1	14	2.75-3.5	4-5	4-5	.02/ .6-.9	977	1038
Ni 1a	14	"	"	4-5	.02/.06	977	1077
Ni 2	7	"	"	2.5-3.5	.02/.06	971	999
Ni 3	-	"	"	0.5	.02/.06	982	1038
Ni 4	-	1.5-2.2	3-4	1.5	.02/.06	982	1066
Ni 5	19	.03	9.75 -10.5	-	.02/.10	1079	1135
Ni 6	-	-	-	-	10-12/.10	877	877
Ni 7	14	.01	0.1	.2 +.04 Mn	9.7-10.5/ .08	888	888
Ni 8	4-5 Cu	-	6-8	21.5-24.5 Mn	.02/.14	982	1010

COPPER AND COPPER ZINC GROUP

IS Classi- cation	X Cu X	X Zn X	X Sn X	X P X	X Pb X	X Al X	X Si X	Solidus X	Liquidus X
	%	%	%	%	%	% max	%	C	C
Cu 1	99.9 min.	-	-	.075	.02	.01	-	1083	1083
Cu 1 a	99 min.	-	-	-	-	-	-	1083	1083
Cu 2	86.5 min.	-	-	-	-	-	-	1083	1083

Table 2.2(b) Compositions of BNi, BCu filler metals

26.3Cr-5.1Si-3.0P-Bal.Ni, 14.8Cr-8.0Si-3.0P-3.0Fe-Bal.Ni¹².

These alloys are developed by modifying ternary Ni-Cr-Si alloys, and can be used in similar manner as a commercial filler metals.

2.2 Roles of fluxes

The primary purpose of brazing fluxes is to promote wetting of the base metal by the braze filler metal by providing clean metal surface. Fluxes are prepared from various chemical compounds. When fluxes are heated to the brazing temperature, reactions may take place between the various flux ingredients, braze filler metal and substrate material forming new compounds, which are different chemically and physically from the unreacted constituents. For instance, presence of fluoborate in the flux may lead to formation of fluorides as the ingredients react.

Commonly used and tested brazing fluxes are summarized in Table 2.3. Survey on the oxide film removal by the use of fluxes was provided by D. R. Milner¹³ with special reference to removal aluminium oxide film in brazing aluminium metal. Sheum West after suggested that alumina is in fact virtually insoluble in all the fluxes, Jordan and Milner showed that flux removal was electrochemical in nature, with the aluminium acting as an anode, the oxide film as a cathode, and the flux as an electrolyte. Aluminium goes into solution, as Al^{+3} ions at the oxide/metal junction Fig.2.1, thus undermining the oxide/metal which, being in compression on the surface, on release curls up, causing the cell to travel along the interface.

At the cathode, the current is maintained by the removal of

AWS ing Flux e No.	Recommended base metals	Recommended filler metals	Recommended useful temp. range	Ingredients	Forms duplied
1	All brazable aluminum alloys (See appendix)	BA1Si	700-1190F 371- 643C	Chlorides Fluorides	Powder
2	All brazable magnesium alloys (See appendix)	BMg	900-1200F 482- 649C	Chlorides Fluorides	Powder
3A	All except those listed under 1,2, and 4	BCuP, BAg	1050-1600F 566- 871C	Boric acid Borates Fluorides Fluoborates Wetting agent	Powder Paste Liquid
3B	All except those listed under 1,2, and 4	BCu, BCuP, BAg, BAu, RBCuZn, ENi	1350-2100F 732-1149C	Boric acid Borates Fluorides Fluoborates Wetting agent	Powder Paste Liquid
4	Aluminum bronze, aluminum brass and iron or nickel base alloys containing minor amounts of Al and (or Ti)	BAg (all) BCuP (Copper base alloys only)	1050-1600F 566- 871C	Chlorides Fluorides Borates Wetting agent	Powder Paste
5	All except those listed under 1,2, and 4	Same as 3B(ex- cluding, BAg-1 through -7)	1400-2200F 760-1204C	Borax Boric acid Borates Wetting agent	Powder Paste Liquid

Table 2.3 : Fluxes for brazing

electrons by oxygen, which then reacts with aluminium ions, at a distance from the cell, to form aluminium oxide. Cell mechanism requires oxygen from the atmosphere to be transferred through the flux to depolarize the oxide cathode. However, the only method of oxygen transfer is one of a combination of convection and diffusion, which should continue after the oxide has been removed. A process of reoxidation followed by oxide removal should therefore take place continuously. Whilst this mechanism of oxide removal is probably specific to the case of aluminium, the inability of the flux to provide protection from reoxidation may occur in all cases.

The above anomaly of the flux action has been resolved by the work of Wall and Milner¹⁴ in 1961, according to their investigation, the surface oxide film is punctured, wetting and spreading take place effectively, as long as surface is not rapidly reoxidized. The penetration of oxide by the liquid metal, and spreading along the oxide/metal interface.

In some instances, however, complex reactions may occur between the molten flux, atmosphere, work and filler metal. Instead of surface being cleaned, these reactions may induce a layer to form over the surface as so inhibit wetting and spreading. For example Cheasten and Sloboda³ reported that when stainless steel is brazed with the aid of a fluoride containing flux e.g. mixture of KBO_2 and KBF_4 . The following reactions might occur.

(i) The flux readily dissolves the protective film of Cr-oxide

from the surface.

- (ii) As a result, Chromium in the underlying steel immediately reoxidised by oxygen diffusing across the flux layer.
- (iii) As a result of the rapid attack caused by two reactions, a finely divided residue of iron builds up on the surface and is converted into fluoride by fluoride-containing constituents in the flux.

To avoid above reactions and to keep work clean, the flux with minimum or without fluoride containing constituent can be used in brazing of stainless steel.

2.3 Brazing in controlled atmosphere

Controlled atmospheres are used extensively for high temperature brazing. They have several advantages over fluxes¹⁵.

- i. A clean, oxide free joint is obtained and the brazement can often be used in the as brazed condition.
- ii. Controlled atmosphere brazing is particularly useful in joining complex assemblies such as heat exchangers, thrust chambers, and honeycomb sandwich structures from which complete removal of flux is difficult or impossible.
- iii. Problems associated with flux entrapment in the brazed joint can be avoided.

Some of the compositions of controlled atmospheres recommended for brazing are presented in Table 2.4.

H_2 is one of the most active agents for reducing the oxides of many metals during brazing. If an oxidized metal is heated to a sufficiently high temperature in a dry atmosphere, the oxide

Source	Maximum dew point incoming gas	Approximate Composition, %				Application		Remarks
		H ₂	N ₂	CO	CO ₂	Filler metals	Base metals	
Combusted fuel gas (low hydrogen)	Room temp.	5-1	87	5-1	11-12	BAg, * BCuP, RBCuZn	Copper, brass*	
Combusted fuel gas (decarburizing)	Room temp.	14-15	70-71	9-10	5-6	BCu, BCuP, * RBCuZn, BCuP	Copper, * brass, * low-carbon steel, nickel monel, medium carbon steel\$	Decarburizes
Combusted fuel gas, dried	-40F (-40C)	15-16	73-75	10-11		Same as 2	Same as 2 plus medium and high-carbon steels, none, nickel alloys	
Combusted fuel gas, dried	-40F (-40C)	38-40	41-45	17-19		Same as 2	Same as 2 plus medium and high-carbon steels	Carburizes
Dissociated ammonia	-65F (-54C)	75	25			BAg, * BCuP, RBCuZn	Same as for 1,2,3,4 plus alloys containing chromium+	
Cylinder hydrogen	Room temp.	97-100				Same as 2	Same as 2	Decarburizes
Deoxygenated and dried hydrogen	-75F (-59C)	100				Same as 5	Same as 5 plus cobalt, chromium, tungsten + alloys and carbides+	
Dehydrated volatile materials	Inorganic vapors (i.e., zinc, cadmium, lithium, volatile fluorides)					BAg	Brasses	Special purposes May be used in conjunction with 1 thru 7 to avoid use of
Purified inert gas	Inert gas (e.g. helium, argon, etc.)					Same as 5	Same as 5 plus titanium, zirconium, hafnium	Special purposes Parts must be very clean and atmosphere must be pure

Table 2.4: Atmospheres for brazing

will be reduced and water vapour will form. Oxide reduction continues until the amount of water vapour increases to the point where H_2O/H_2 ratio reaches equilibrium for the metal oxide at the particular temperature.

Further oxide reduction will occur only when the moist H_2 is replaced by dry H_2 . Although all metal oxides can be reduced, some are more difficult to reduce than others i.e., H_2 with a much lower dew point at a given temperature is required before oxide reduction can occur. Dew point is a measure of the water content in H_2 atmosphere i.e. dryness of atmosphere. Fig.2.2 shows how water vapour content and dew point are related over the range in which H_2 normally used for brazing¹³.

In fig.2.2 curves are given for different metal oxides, showing how for each the equilibrium dew point varies with the temperature. The region above and to the left of each curve represents conditions that are oxidizing to metal, and all points below and to the right of each curve cover the conditions required for reducing the oxides. For instance, one would expect to require H_2 with a dew point of about $-35^{\circ}C$ to achieve equilibrium in the reducing reaction at a temperature of $1000^{\circ}C$, and dew point of about $-20^{\circ}C$ at the brazing temperature of $1200^{\circ}C$ for chromium containing steels.

Although in theory it is possible to reduce any oxide with H_2 which is sufficiently dry, in practice the more stable oxides may require such vast quantities of dry H_2 as to be inconceivable.

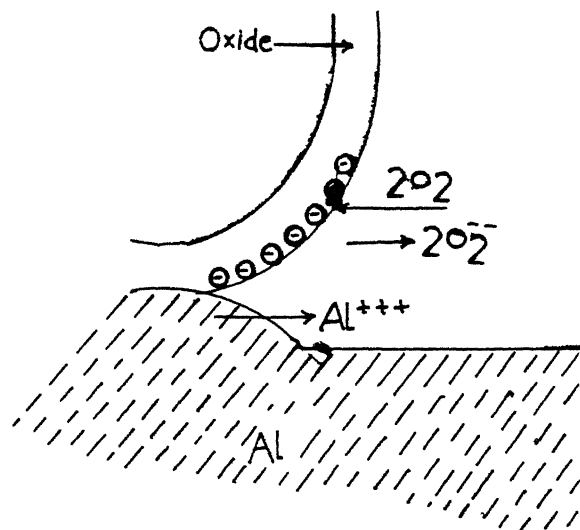


Figure 2.1 The mechanism of removal of aluminum oxide by molten flux

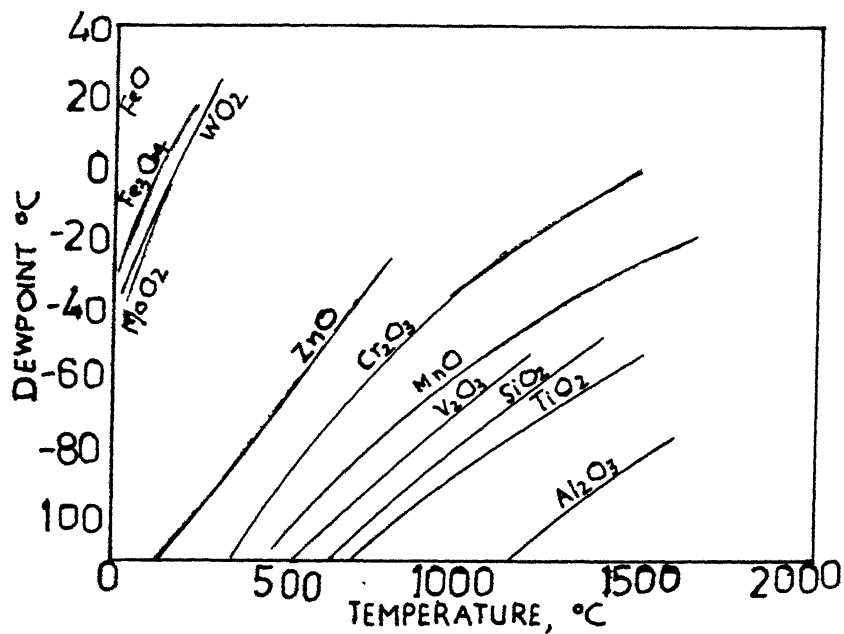


Figure 2.2 Relation of hydrogen dewpoint to equilibrium temperature for reduction of various metal oxides in hydrogen.

2.4 Vacuum (fluxless) brazing

Another method of obtaining a clean metal surface is to heat the metal in vacuum. Vacuum brazing is particularly well suited for joining (a) heat-resistant Ni and Iron base alloys that contain Al and/or Ti which form stable oxides (b) vacuum reactive metals, and (c) refractory metals.

Vacuum removes essentially all gases from the brazing area, thereby eliminating the necessity of purifying a supplied atmosphere. The mechanism of oxide removal in vacuum is not clearly understood. Oxide films can be removed by evaporation, dissociation, diffusion, or a combination of diffusion and chemical reaction. The first possibility, that of oxide being dissociated to form oxygen and metal, is not feasible since equipment is required to operate at pressures much below about 10^{-5} mm. Hg, for most of the metals, and at normal brazing temperatures this might not be feasible¹⁶. In the case of Ti, the very poor vacuum which will suffice is even more inconsistent with the theory of dissociation. Here, however, the great affinity of Ti for oxygen at elevated temperatures provides the obvious explanation that, in vacuum, the Ti absorbs oxygen from its oxide.

Studies on wetting and spreading phenomena in vacuum by wall and Milner¹⁴ in 1961 lead to following conclusions.

- (i) A liquid metal can in certain circumstances spread on a base metal that is covered with oxide by the processes of penetration of the oxide by liquid metal and spreading

along the oxide/metal interface.

- (ii) Penetration require that the solid substrate is soluble in the liquid metal and is enhanced by increased temperature. In systems where spontaneous penetration does not occur, the same effect, can be achieved by artificially establishing metal-to-metal contact. Spreading along the oxide/metal interface necessitates some solubility of the solid metal in the liquid metal, yet wide solubility would favour erosion rather than spreading.
- (iii) For a pure metal which can dissolve its own oxide there is a critical rate of arrival of oxygen at the surface, below which the surface becomes and remains substantially oxide free. This rate of arrival governs the "Critical Pressure" for brazing. Vacuum brazing of pure metals and alloys containing small proportions of an element that form stable oxide must be performed below the critical oxygen pressure. If, however, artificial penetration can be ensured by some means such as joint design, then the scope of vacuum and inert gas brazing is extremely wide.

CHAPTER THREE

PLAN OF THE PRESENT WORK

Besides making a critical review of the literature, efforts have been made in the present work to study the effects of reactions that may occur between the various fluxes, stainless steel substrate and atmospheric air, on the wetting behaviour of the substrate by copper-silver and copper-silver-tin alloys. The laboratory studies mainly consisted of the following:

1. Fabrication of a high temperature silicon carbide box furnace.
2. Preparation of copper-silver and copper-silver-tin alloys for wetting experiments.
3. Design and performances of experiments for measuring changes in weight of metal strip under various conditions:
 - (a) Stainless steel plate in air.
 - (b) Flux on stainless steel substrate.
 - (c) Stainless steel strip dipped in the flux.
 - (d) Stainless steel strip partially dipped in the flux and partly exposed to air.
4. Development of technique to melt the various flux ingredients.
5. Area of spread tests using silver brazing and synthetic flux.
6. Contact angle measurements for the drops using optical

microscope.

7. Fabrication of the facilities to carry out the wetting study in nitrogen gas atmosphere.
8. Dip coating experiments to observe the changes in surface appearance.
9. Design of electrochemical cell for cell measurement studies.
10. Analysis of bands around the spread drop and coatings.
11. Analysis of the results using thermodynamic data.

CHAPTER FOUR

EXPERIMENTAL PROCEDURE

4.1 EQUIPMENT

4.1.1 Furnaces

(a) Silicon Carbide Box Furnace

A box furnace with outside dimension of (355mm x 381mm x 457mm) with heating zone of (127mm x 127mm x 381mm) was fabricated to provide a temperature of 1000°C or so. Four Silicon Carbide rods of 455mm length and 12 mm diameter and hot zone length of 100mm provided the source of heat. Power to the furnace was supplied by 25kVA oil cooled type transformer where output could be changed in steps of 5V in the range of 55V to 110V. The power was supplied in parallel to a combination of two rods such that the maximum current through each rod does not exceed 15 Amp.

The temperature of the furnace was controlled with an on-off type controller using Pt-Pt+10%Rh thermocouple. Another Chrome-Alumel thermocouple was used to measure temperature near the sample using a temperature indicator. Section view of the furnace is given in fig.4.1.

(b) Vertical Silicon Carbide Furnace

A fabricated furnace with cylindrical heating zone of 60mm diameter and 270mm long was used to provide a temperature upto 1400°C . Six Silicon Carbide rods of 455mm length and 12mm diameter, connected in series, provided the source of heat.

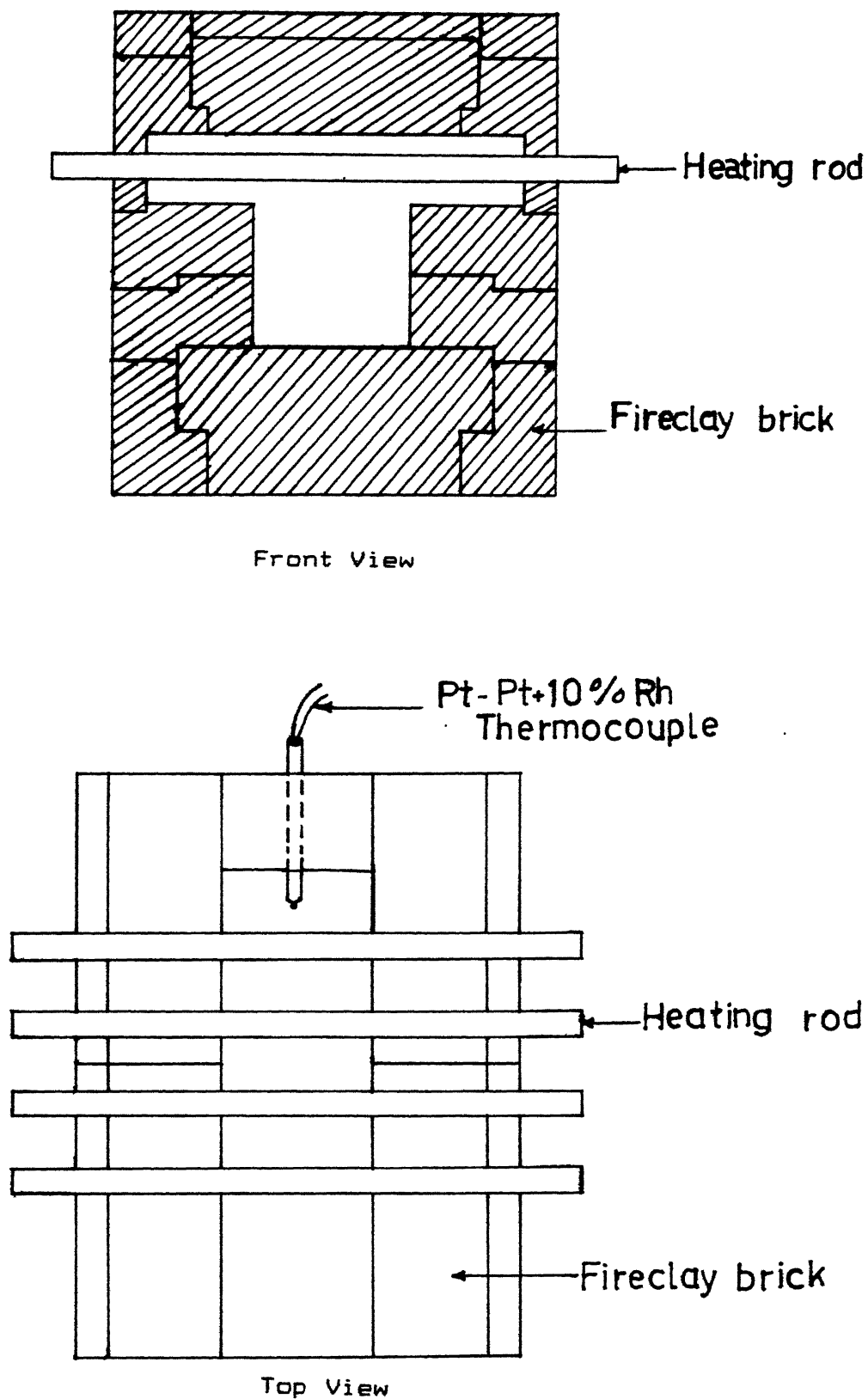


Figure 4.1 Section view of the Silicon Carbide box furnace

Power to the furnace was supplied by 40 Amp and 0-250V single phase oil cooled type transformer. The temperature of the furnace was controlled to $\pm 2^{\circ}\text{C}$ with on-off type controller using Pt-Pt+10%Rh thermocouple.

(c) Molybdenum-Disilicide Furnace

The 70C5 model horizontal electric furnace was supplied by Bysakh & Co., Calcutta, capable of providing a maximum temperature 1700°C using Molybdenum-disilicide heating elements (super kanthal). The temperature of the furnace was controlled by PI/PID type solid state temperature controller using (Pt-6%Rh/Pt-30%Rh) thermocouple.

4.1.2 Optical Microscope

A microscope with attached camera, supplied by WILD Company of Switzerland, was used to take photographs for contact angle measurements.

4.1.3 Electronic Balance

An automatic microbalance was used to measure all masses to an accuracy of 0.1 mg.

4.1.4 Scanning Electron Microscope

JSM-B40A Scanning Microscope which was supplied by JEOL, JAPAN along with Kevex analyst, supplied by California, U.S.A. Company, was used for composition measurements by energy dispersive spectrometer (EDS) analysis.

4.1.5 Multimeter

A Philips PM2718, autoranging multimeter with 4+1 digit liquid crystal display and with high DC accuracy (0.05%), 100kHz AC measurements capability, was used for voltage and current measurements.

4.2 MATERIALS

4.2.1 Pure Metals

Commercial grade pure Silver, Pure Copper and pure tin were used for the experiments.

4.2.2 Stainless Steel

Commercial grade Austenitic stainless steel sheet of 1.6 mm thickness was used for making the plates (40mm x 40mm x 1.6 mm) for welding study and strips (20mm x 10mm x 1.6 mm) for dipping and cell measurements.

4.2.3 Fluxes

(a) Silver Brazing Flux

Commercial flux named Silverotectic, which was supplied by A.V.S. Products (India), New Delhi, was used for the experiments.

(b) Certain synthetic fluxes were made in the laboratory using the following materials:

(i) Borax

LR grade disodium tetraborate having chemical formula $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and molecular weight of 381.38 was used

(ii) Boric Acid

LR grade boric acid having chemical formula H_3BO_3 , supplied by Polypharm Pvt. Ltd., Bombay was used.

(iii) Potassium Chloride

LR grade potassium chloride (KCl), which was supplied by Thomas Baker (Chemicals) Pvt. Ltd., Bombay was used.

The physical properties of the pure metals and flux ingredients are given below¹⁷:

Sr.No.	Name	Molecular weight	Density	Melting Point (°C)
1.	Cu	63.5	8.96	1083
2.	Ag	107.8	10.5	960
3.	Sn	118.7	5.75	231.9
4.	KCl	74.5	1.98	776
5.	Borax	381.3	1.73	741
6.	Boric acid	61.8	1.43	395

4.3 PROCEDURE

4.3.1 Flux Making

Potassium chloride, Borax and Boric Acid were first melted separately in quartz tubes. The solidified masses were removed by breaking the quartz tube and were mixed in certain proportion to make fluxes of desired composition.

4.3.2 Alloy Preparation

Five grade alloys of different compositions were made by melting copper, silver and tin in certain proportions in quartz tube using vertical silicon carbide furnace and sucking the melt into 4mm quartz tube. Composition of prepared alloys are given below:

Sr. No.	Alloy Composition (wt%)			Melting range (°C)
	Cu	Ag	Sn	
1	30	60	10	610-720
2	75	25	0	779-970
3	50	50	0	779-860
4	28	72	0	779
5	0	100	0	960

4.3.3 Precleaning

Stainless steel plates and strips were cleaned first with 410 grade emery paper and water. Secondly plates and strips were cleaned by dipping in ($1\text{H}_2\text{SO}_4:1\text{HCl}:8\text{H}_2\text{O}$) solution. After dipping plates and strips were washed in running water.

4.3.4 Wetting Experiments

Wetting experiments were carried out by keeping weighed amount flux on cleaned stainless steel plate and then the plate was inserted into the furnace, which was already heated to the required temperature. After the flux was melted weighed amount of prepared alloy was kept at the centre of the plate. Two minutes after alloy was melted, the plate was allowed to cool below the melting point of alloy before it was taken out of the furnace and quenched in running water for cleaning. In some experiments the time lag between the melting of flux and adding the filler metal was varied to see the effect of flux reactions on the wetting behaviour.

4.3.5 Measurement of Areas of Spread

Measurement was carried out by taking photograph of the solidified drop and measuring area using tracing paper and graph paper. In some cases the area of spread was very large as the thickness of droplet was less than 1 mm, the area could be measured directly on the plate using a tracing graph paper.

4.3.6 Contact Angle Measurement

Contact angle was measured by cutting section of the

solidified drop on the plate and taking photograph of the section.

4.3.7 Weight Change Study

Weight change in stainless steel plate on heating with and without flux on it was carried out at different time and temperatures, using a box silicon carbide furnace.

Weight change in stainless steel strips was also determined by dipping it into fluxes at different time and temperatures. In some experiment alumina crucible (35mm diameter, 32 mm height) was used to hold the molten flux in the box furnace and the stainless steel strips were partially or completely dipped in it using a metal wire. In another series of experiments the flux was melted in sillimanite (15mm I.D., 310mm long) tube heated in the vertical silicon carbide furnace and the stainless steel strips were dipped to the desired level using the platinum wire. The flux was removed from the strips after the experiment by washing in running water before weighing.

4.3.8 Composition Analysis

Attempts were made to determine composition of the bulk and the bands which appear at the edge of the spread drop of different alloys by EDS analysis using scanning electron microscope. The sample was first tested with the prepared alloys. In some cases the coating obtained on the strip during dipping experiments was also analysed.

4.3.9 Electrochemical Cell Measurements

The possibility of electrochemical deposition of silver on stainless steel strip in the presence of molten flux was examined by setting up the cell shown in Fig. (4.2). Sillimanite tube was used to melt the prepared flux and stainless steel strip and liquid silver beneath the flux were electrodes. A insulated platinum wires were used to make contact with the electrodes. Open circuit voltage and short circuit current responses were measured using multimeter.

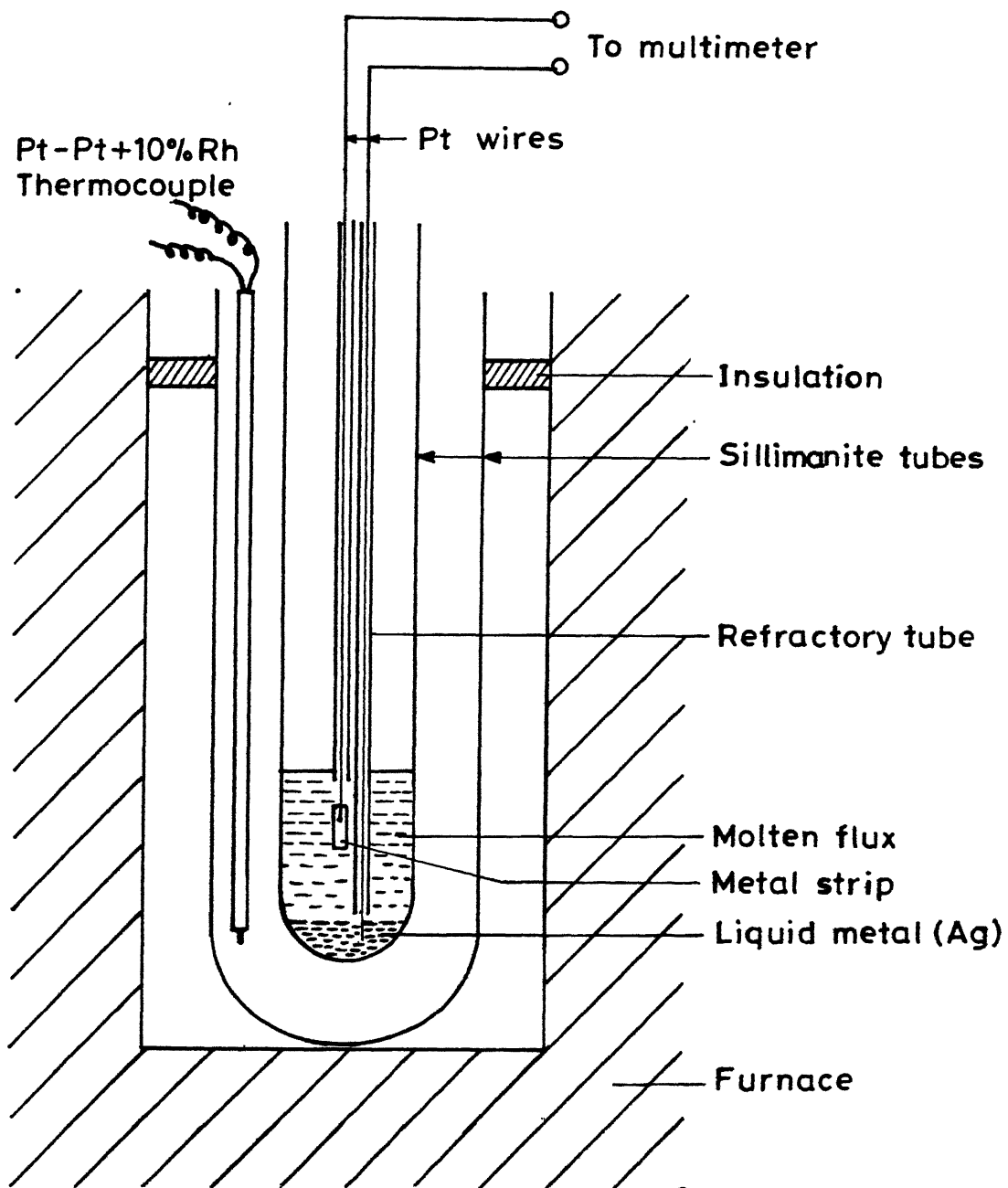


Figure 4.2 Section view of the electrochemical cell

CHAPTER FIVE

EXPERIMENTAL RESULTS

5.1 WEIGHT LOSS EXPERIMENTS:

The various categories of experiments performed are schematically shown in Fig. 5.1 and the results of which are given below.

5.1.1 Heating of Stainless Steel in Air-(WLA)

Experiments were carried out to measure the weight changes in stainless steel strips upon heating in air in the furnace for certain length of time.

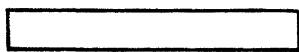
Results showed that gain in the weight of about 7 gm of stainless steel strip was less than .004 gm (.05%) even after heating at 800°C for a period of 30 mins. At 600°C or lower temperature, the change in weight was less than 0.002gm (.02%) after the 30 minutes.

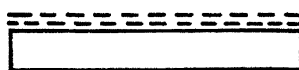
5.1.2 Heating of Stainless Steel Plate with Silver Brazing Flux-(WLB)

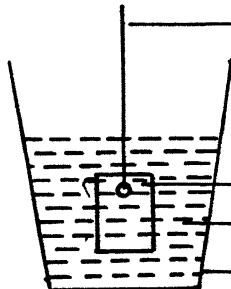
In this category experiments were carried out by heating the stainless steel plate with about 1 gm of commercial flux on it in the furnace at 770°C for different lengths of time to measure any changes in the weight and appearance of plate due to the flux-substrate reactions. The following observations were made.

WEIGHT LOSS EXPERIMENTS

CATEGORY

WLA  — Stainless Steel plate

WLB  — Flux
— Stainless Steel plate

WLC  — Support wire
— Metal strip
— Flux
— Alumina crucible

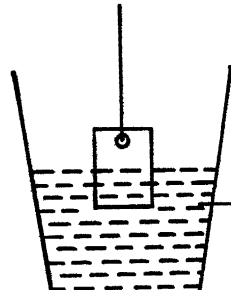
WLD  — Flux

Fig. 5.1 Schematic representation of categories of weight loss experiments

- a) For heating upto 5 mins in the furnace at 770°C followed by rapid cooling, the flux could be removed by washing in running water. The substrate beneath the flux remained clean and loss in its weight was around .38%.
- b) For heating upto 10 mins in the furnace at 770°C , solidified flux could be removed after prolonged washing in running water. The substrate got blackened and there was a net weight loss of around 1%. For heating upto 20 mins, similar results were obtained and the weight loss of 1.4%.

5.1.3 Dipping Experiments in Molten Fluxes-(WLC)

In this category reactions between the substrate material and the molten fluxes were studied by measuring the changes in the weight and appearance of the strips, when dipped completely in the molten flux. Results obtained are summarised in Table 5.1.

Time of dipping was kept 30 mins for all the experiments in this category. There was no blackening of the substrate unlike the WLB category of experiments. Flux could be removed easily by washing in running water after the experiments except when using Borax flux (WLC5) experiment. The flux became glassy upon solidification and could be removed mechanically but not by washing alone in this case.

In some experiments the commercial flux was heated alone in the alumina crucible and changes in its weight were measured at various temperatures. The flux underwent a loss of 3.36% when heated at 200°C for 30 mins. It further experienced losses of

Table 5.1**Weight Loss Data From Dipping in Molten Fluxes Experiments**

Time of dipping = 30 mins

Experiment No.	Flux Used	Strip Material	Temperature (°C)	Weight loss(%)
WLC1	Silver brazing	Stainless	700	.28
WLC2	Silver brazing	Stainless	800	.47
WLC3	Borax	Stainless Steel	800	.11
WLC4	90% Boric Acid, 10% Potassium Chloride	Stainless Steel	1000	3.00
WLC5	90% Boric Acid, 10% Potassium Chloride	Copper	1000	11.4

.78% at 400°C, 0.13% at 600°C, followed by 0.33% at 800°C for 30 mins duration of heating at each temperature.

5.1.4 Partial Dipping Experiments in Silver Brazing Flux-(WLD)

In this category a few experiments were carried out to highlight further the role of atmospheric oxygen in the flux-metal reactions. The stainless steel strip was partially dipped in the silver brazing flux and partially remained outside the flux. It was observed after a period of 20 mins at 800°C that the undipped part got blackened while the dipped part remained clean and bright and the loss in weight of strip after washing was around 0.76%.

5.2 AREA OF SPREAD TESTS

5.2.1 Wetting with Silver Brazing Flux-(ASA)

In this category wetting experiments were carried out using 60Ag-30Cu-10Sn filler metal and commercial grade silver brazing flux. The temperature was varied from 700-850°C and the time lag between melting of flux and addition of the filler metal was varied from 0 to 25 mins. Results are given in Table 5.2. The width of the band observed around the spread mass in each experiment is also mentioned in the Table 5.2.

5.2.2 Wetting Tests with Prepared Fluxes-(ASB)

In this category, wetting experiments were carried out with 72Ag28Cu filler metal and prepared fluxes of various compositions at temperature 850°C. There was no blackening of the plate as observed in WLB category and also ASA3, ASA4, ASAB, ASA10 and ASA12 experiments. Results obtained are summarised in Table 5.3.

Table 5.2**Results of Area of Spread Tests in ASA Category of Experiments**

Filler Metal used = 60Ag-30Cu-10Sn

Experiment No.	Temp °C	Time Lag (Mins)	Area of Spread (cm ²)	Halo or Band Width (mm)	Appearance of Plate
ASA1	750	0.0	2.2	1-2	Clean
ASA2	750	10.0	0.60	<1	Clean
ASA3	750	15.0	0.22	-	Black
ASA4	750	20.0	DNW*	-	Black
ASA5	770	0.0	2.53	2	Clean
ASA6	770	2.0	2.26	1-2	Clean
ASA7	770	5.0	0.85	<1	Clean
ASA8	770	10.0	DNW*	-	Black
ASA9	800	5.0	0.78	<1	Clean
ASA10	800	10.0	DNW*	-	Black
ASA11	850	2.0	1.47	<1	Clean
ASA12	850	5.0	DNW*	-	Black

* Did not wet

Table 5.3**Results of Wetting Tests with Prepared Fluxes**

Temperature of the experiment = 850°C

Filler metal used = 72Ag-28Cu

Experiment No.	Flux Composition			Area of Spread cm ²	Appearance
	Borax wt%	Boric Acid wt%	KCl wt%		
ASB1	100	0	0	DNW*	Black
ASB2	90	0	10	0.08	Clean
ASB3	60	30	10	0.25	Clean
ASB4	60	20	20	0.33	Black spots
ASB5	50	50	0	DNW*	Black
ASB6	40	40	20	0.46	Black spots
ASB7	30	60	10	0.59	Clean
ASB8	25	75	0	DNW*	Clean
ASB9	00	100	0	DNW*	Clean
ASB10	00	90	10	2.8	Clean

* Did not wet

5.2.3 Wetting of Stainless Steel by Copper-Silver Alloys-(ASC)

Based on the results of ASB category of experiments, the flux containing 90% boric acid and 10% KCl was chosen to test the wetting characteristics of the stainless steel substrate by the braze filler metals of different grades of copper-silver binary alloys. The contact angle and area of spread were measured after solidification as discussed in chapter four. Results are summarised in Table 5.4. Wetting was observed in all cases and the flux could be removed after washing. In all the cases the bands were observed around the spread mass and widths of the bands are mentioned in the Table 5.4.

5.3 Results of Cell Measurements-(ECC)

As mentioned in section (4.3.9), the electrochemical cell had two electrodes consisting of stainless steel strip and the liquid silver separated by molten flux. During short circuiting of electrodes using pt-lead wires, no current could be measured. The open circuit voltage measured across the electrodes and the changes in appearance of strip after the experiment are summarized in Table 5.5.

Table 5.4

Results of Wetting Study of Stainless Steel Substrate
by the Copper-Silver Alloys using 90% Boric acid, 10% Potassium
Chloride Flux

Experiment No.	Filler Metal Cu wt%	Metal Ag wt%	Temp. of Exp. °C	Area of Spread cm ²	Band Width (mm)	Contact Angle (deg.)
ASC1	100	0	1120	5.23	1-2	19
ASC2	75	25	1000	1.79	1	45
ASC3	50	50	1000	2.49	3-4	29
ASC4	28	72	1000	2.75	2-4	25
ASC5	0	100	1000	4.31	1	21

Table 5.5**Results of Cell Measurements**

Temperature of the experiment = 1050°C

Composition of the flux = 90% Boric Acid, 10% Potassium Chloride

Time of the experiment = 30 mins.

Experiment No.	Distance between electrodes (cm)	Open Circuit Voltage (volts)	Appearance
ECC1	3.0	(.8-.9)	Clean
ECC2	2.5	(.4-.6)	Clean
ECC3	2.0	(.2-.35)	Bright
ECC4	1.0	(.4-.6)	Bright

5.4 Dip Coating Experiments-(DCE)

In this category, the metallic strip dipped in the molten flux (90% Boric acid, 10% potassium Chloride), was not allowed to come in contact with the liquid metal kept beneath the molten flux in the refractory tube as shown in Fig.4.2. The coating observed on the strips was analysed using scanning electron microscope. The results are summarised in Table 5.6. In experiment DCE1 and DCE3, the stainless steel and copper strip appeared to be bright. The DCE2 experiment the stainless steel strip was found to be reddish which matched with the findings of SEM analysis.

5.5 SEM ANALYSES

Composition of the filler metal as well that of the bands observed on the stainless steel plate were measured using scanning electron microscope. Results obtained are summarized in table 5.7. IN ASC3 and ASA5 experiments band was analysed at two places one closer to the spread mass and the other near the end of band.

Table 5.6**Results of Dip Coating Experiments**

Flux used = 90% Boric Acid, 10% Potassium Chloride

Temperature of Experiments = 1000°C

Time of dipping = 30 mins

Experiment No.	DCE1	DCE2	DCE3
Temperature	1000°C	1100°C	1000°C
Strip material	Stainless Steel	Stainless Steel	Copper
Liquid Metal	Silver	Copper	Silver
Coating Composition	wt%	wt%	wt%
Cu	-	82.6	99.2
Fe	82.0	7.0	-
Ni	9.8	9.0	-
Cr	9.0	0.9	-
Ag	0.35	-	0.8

Table 5.7

Results of SEM Analysis of Wetting Experiments

Experiment No.	ASC4		ASC3			ASA5		
Elements	Bulk analy- sis	Band analy- sis	Bulk analy- sis	Band1 analy- sis	Band2 analy- sis	Bulk analy- sis	Band (near the edge) %	Band (awa for edge) %
	%	%	%	%	%	%	%	%
Cu	26.7	10.4	34.3	26.4	27.8	44.2	43.8	38.3
Ag	73.3	35.1	65.7	51.9	65.9	43.6	51.9	56.8
Fe	-	39.1	-	14.3	6.3	1.6	0.6	-
Cr	-	9.5	-	2.0	-	-	0.2	-
Ni	-	5.9	-	5.4	-	-	-	4.9
Sn	-	-	-	-	-	10.6	3.5	-

CHAPTER SIX

DISCUSSION

6.1 Commercial Flux

Results obtained in the present study show that the brazing flux available in the market promotes wetting of stainless steel substrate by copper-silver alloys by providing a clean metal surface. The solid metal-liquid filler metal must have lower interfacial energy value than the solid-flux interfacial value and the system lowers its energy by spreading of filler metal on the clean solid surface. The efficiency of flux in providing a clean surface is retarded by increasing the time of contact between the flux and solid. The flux is known to have melting point of 500°C . It was found to undergo changes in its weight due to removal of 2 to 3% moisture but thereafter it remained more or less stable at temperature upto 800°C , when heated alone in the alumina crucible. In presence of stainless steel substrate and atmospheric air, the flux however underwent rapid changes in its appearance as shown in WLB category of experiments and the liquid filler metal did not wet the material as shown by the results in Table 5.2. The results obtained may be attributed to the following factors.

- (i) The impervious and coherent chromium oxide layer, on the surface of stainless steel, imparts the corrosion resistance properties to stainless steel. This layer is however detrimental to the wetting as it lowers the solid gas interfacial energy and it can not be replaced by

solid-liquid interface. The oxidation resistance of stainless steel was shown to be maintained at 800°C as borne out by the results of WLA category of experiments.

- ii) The molten flux is able to dissolve or remove the chromium oxide layer present on the surface to provide a clean metal surface for wetting.
- iii) The flux is not able to protect the clean surface from the atmosphere reoxidation due to diffusion flux of oxygen atoms across the .02 to .03mm thick molten flux layer on the plate. Any reoxidized layer of chromium oxide must be rapidly removed by the flux in order to provide clean metal surface for wetting. This mechanism was first suggested by Chaston and Stoboda³.

The oxygen potential required for reoxidation of chromium may be determined from the following:



$$\log \frac{a_{\text{Cr}_2\text{O}_3}}{a_{\text{Cr}}^2 p_{\text{O}_2}^{3/2}} = \frac{59364}{T} - 13.52$$

Taking activity of chromium as 0.2 in the stainless steel and that of chromium oxide as unity, calculations show that the substrate will be reoxidized if the oxygen pressure exceeds 10^{-27} at 800°C and 10^{-22} atm. 1000°C.

- iv) At higher temperatures, the rate of reoxidation of the clean surface and its subsequent removal by the flux must be higher, and this may shorten the time when the flux is no more capable of absorbing or dissolving the chromium oxide layer. The blackening of the plate flux may be due to

presence of excessive chromium oxide in the flux. This is borne out by the results of Table 5.2.

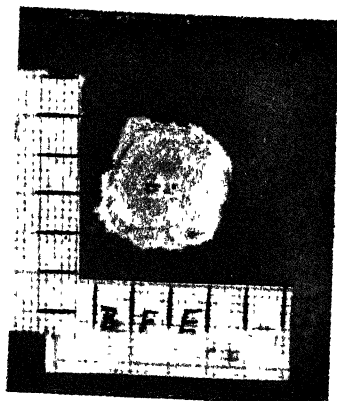
- v) Results of WLC category experiments show that the plate was protected from atmospheric oxygen when dipped completely in the flux. The chromium oxide layer is not reformed after its initial removal and the plate remained clean after the experiment.

Efforts to avoid blackening of the plate by maintaining a flow of N_2 gas above the plate did not meet success as the oxygen partial pressure must still be high in the system for to reoxidation of chromium to take place. In some experiments, charcoal was placed close to the plate and N_2 was passed in the closed assembly. The charcoal was found to be changed to the ash signifying the presence of oxygen flux in the system. New arrangements may be required for the success of such experiments where the oxidation of chromium and hence the blackening of the plate may be avoided.

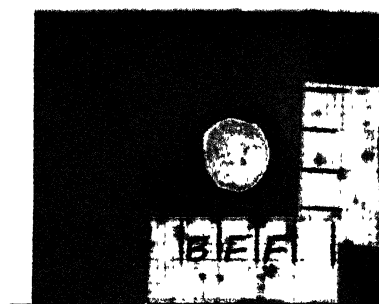
- vi) In the partially dipped experiments (WLD category), the part remaining above the molten flux bath but exposed to flux vapours and atmospheric oxygen rapidly corroded but the part that remaining inside the flux did not undergo any changes. The exact mechanism of corrosive action of the flux vapours on the stainless steel substrate may not be known. A few additional experiments were carried out to test the corrosion behaviour. Two stainless steel plates, one containing the flux on it and the other without any flux on

it were heated side by side in the furnace. The plate with flux on it get blackened as mentioned before. The adjoining plate without flux under went some blackening and there was a net weight gain of 0.3% which may be compared to the negligible weight gain of less than .05% in absence of flux vapours for the same temperature and time of heating as shown in WLA category of experiments. These result also demonstrate the importance of the complete removal of the flux after experiment in order to avoid corrosion of the brazement in service.

One may conclude that the flux is helpful in promoting the wetting as long as it has not reached the saturation point of dissolving the chromium oxide layer. The efficiency of flux decreases rapidly with time especially at high temperatures. The ingredients present in the flux are not known and hence it is not possible to describe the various chemical reactions involving the flux, filler metal and substrate material. These chemical reactions give rise to formation of bands in ASA and ASC experiments. As the flux efficiency to clean the surface decreases, area of spread and the width of band adjoining the spread mass tend to decrease with increasing the time lag of the melting the flux in the substrate and placing the filler metal on it. The experimental results in shown in Table 5.2 agree with this analyses. Photographs in Fig.6.1 show the decrease in area of spread and band width with increased time lag.



(a) 2.0 mins. time lag (ASA6)



(b) 5.0 mins. time lag (ASA7)

Figure 6.1 Photographs of ASA category experiments showing area of spread and bands

6.2 Prepared Fluxes

The brazing fluxes are reported to contain borates, fluoborates, boric acid, chlorides and fluorides besides the wetting agents. Since the chemical composition of the brazing flux was not specified, it was considered useful to carry out a few experiments using synthetic fluxes of known compositions. As mentioned in section 4.3.1 the fluxes ingredients were melted to drive off any moisture and volatiles. The resolidified masses were mixed to prepare the synthetic fluxes. The attempts to make a homogeneous mass of flux by melting the ingredients together in refractory tube did not meet success as there were distinct layers of the ingredients in the solidified mass. The following observations could be made from the results of experiments obtained by using synthetic fluxes.

- (a) Borax rich flux gave a glassy appearance on solidification and it did not let the 72Ag, 28Cu alloy come in contact with the substrate material at 850°C. The molten filler metal droplet remained mobile on molten flux mass and there was no wetting. There must be a thin and viscous layer of the flux beneath the filler metal which prevented the solid-liquid contact.
- (b) The Boric acid also did not promote wetting at 850°C. Similarly any other combination of boric acid and borax did not promote wetting, though they are reported to have the capability of dissolving certain oxide films. It may be concluded from the results obtained in the present study that the borax-boric acid fluxes do not remove the chromic oxide layer effectively.

- c) Addition of KCl either to boric acid or to the binary mixtures of boric acid-borax provided wetting. The best results were obtained with 90% boric Acid-10%KCl mixture as shown in Table 5.3 .
- (d) The synthetic flux mixture on melting was found to remain more or less stable on heating upto 1100°C and there was no blackening of stainless steel substrate observed when heated with flux on it in the furnace at 1000°C for period of 30 mins. This is in contrast to the observations made using commercial flux. The protection of the clean substrate beneath the flux from the atmospheric reoxidation may be attributed to the layering of flux ingredients on the plate. The potassium chloride having high density than boric acid lies at the bottom close to the substrate and boric acid layer above the potassium chloride layer restricts the supply of atmospheric oxygen. The flux mixture thus appears to be quite stable.
- (e) Results of weight loss experiments given in Table 5.1 show that fluxes containing potassium chloride result in weight losses of 3.0 % for stainless steel and 11.4 % for copper strips when dipped in the molten flux at 1000°C for a period of 30 mins.. This may be attributed to the chemical reactions occurring between the molten flux and metal substrate. The reactions are described in the follzowing section.
- (f) The bands or coatings observed around the periphery of the spread mass in the wetting experiments may be attributed to the following.

- (i) Filler metal constituents i.e. silver and copper may go to the flux as metallic ions till the saturation limits are reached.
- (ii) The ions of filler metal constituents in the flux are carried away to the substrate surface ahead of the droplet by the convective currents.
- (iii) The filler metal constituents are then deposited on the substrate by the reverse flux-metal reactions. In soldering, electrochemical reactions have been reported^{4,7} to be important in causing the deposition of tin ahead of the droplet but in brazing simple displacement reactions are found to be fast probably due to much higher temperatures involved.
- (g) All the silver-copper alloys starting from pure copper to silver are found to wet the stainless steel substrate using 90% boric acid and 10% potassium chloride flux. Results plotted in Fig. 6.2 and Table 5.4 show that maximum area of spread or the minimum contact angle is obtained by using pure copper filler metal. In all the cases the interface between the solid and liquid seemed to be sharp. A few representative photographs taken at a magnification of 500 are shown in Fig. 6.3. This signifies that there is not much of alloying taking place between the filler metal and the base metal during the time duration of experiment.

6.3 Thermodynamic analyses of chlorides system:

The standard free energies of formation of various chlorides of metals of interest in the present study are compared in Fig. 6.4 . One may see that potassium chloride is fairly stable

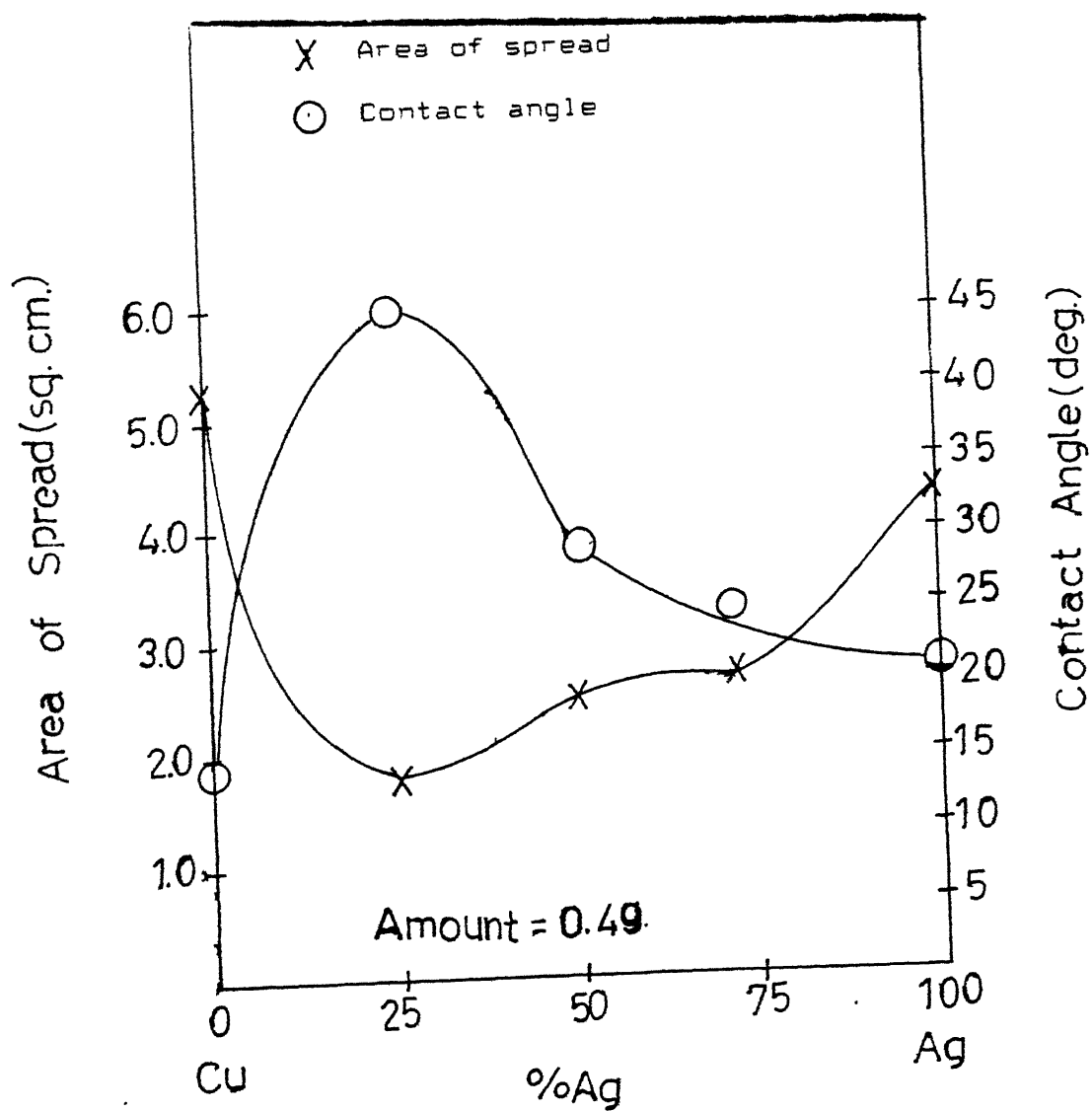


Figure 6.2 Plot of area of spread and contact angle for different copper-silver alloys

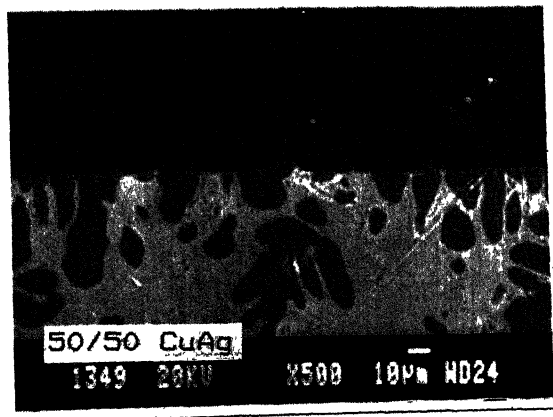
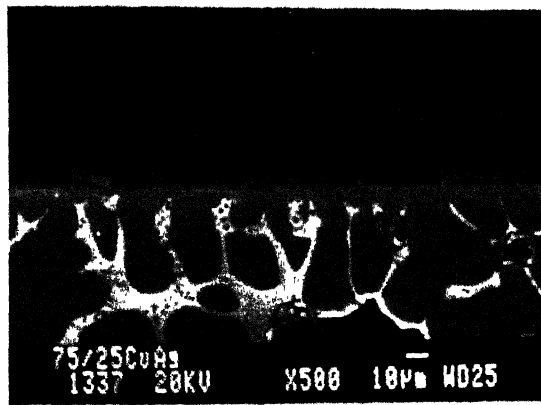
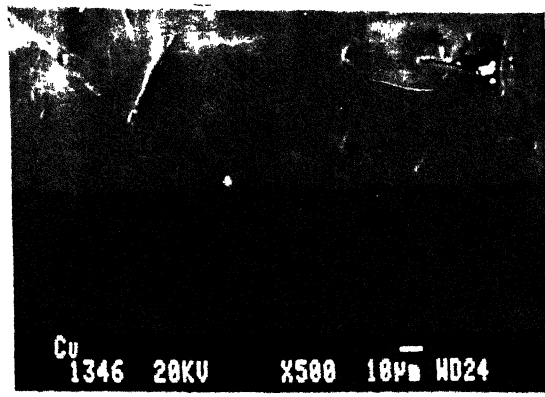


Figure 6.3 Photographs showing the interface between the stainless steel substrate and different filler metals

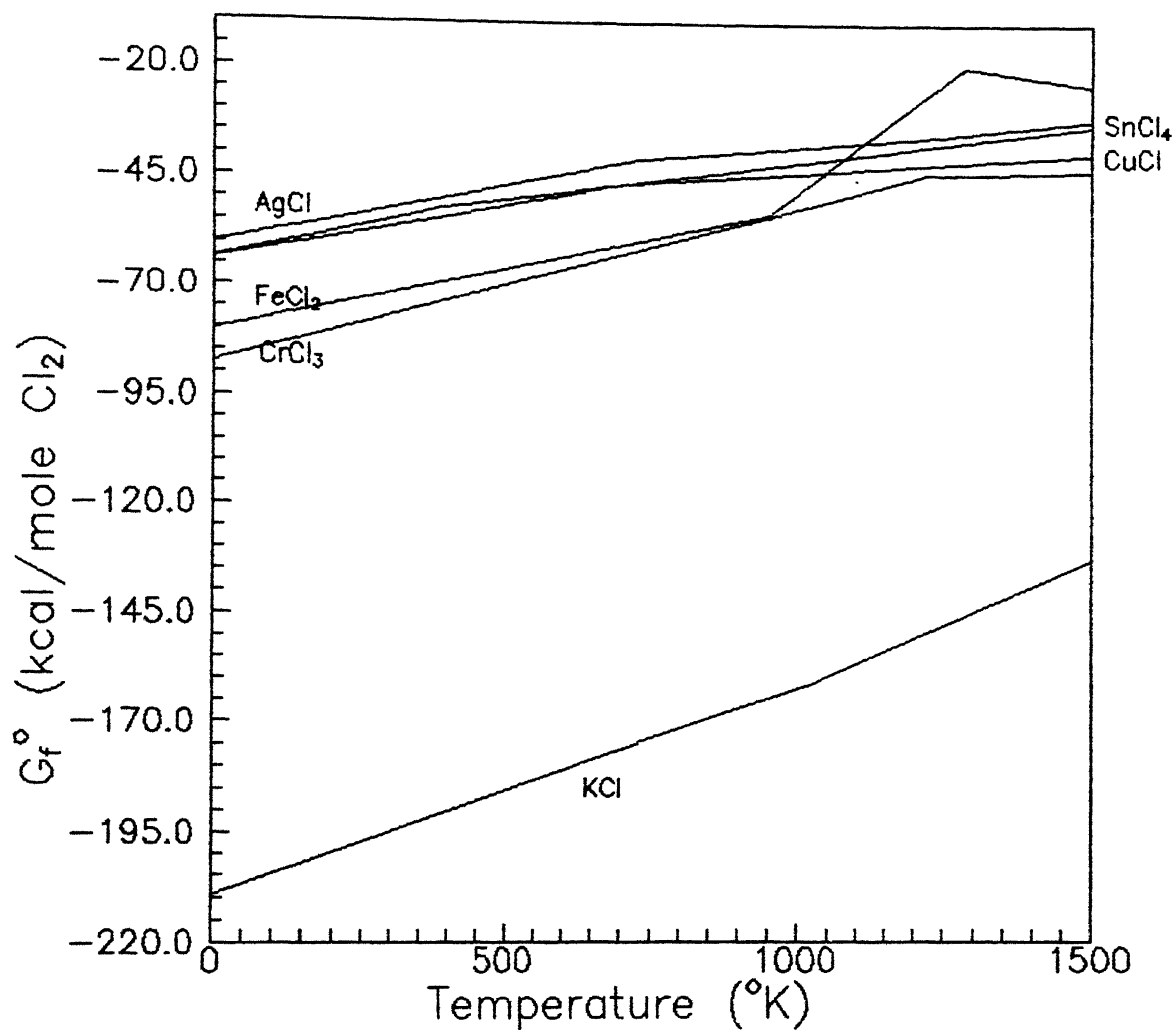


Figure 6.4 Standard free energy of formation of various metallic chlorides

compound and will take part in the reactions to a very limited extent with other elements such as copper, silver, iron, chromium and tin. The reactions and the product of concentrations are summarized in Table 6.1 at the system temperature of 1000°C . Potassium is present as vapours in its standard state at the reaction interface and its partial pressure or activity may not be easy to compute. A look at the table 6.1 shows that CuCl and AgCl have more chances of being formed than that of FeCl_2 , CrCl_3 and SnCl_4 . This is borne out by the results that copper strips experience more weight losses in 90% boric acid, 10% Potassium Chloride flux than the stainless steel strips for the same time and temperature of dipping. Also the appearance of copper reddish surface on the stainless steel strip when dipped in the flux which has been exposed to copper metal confirms that copper goes into the flux easily as a result of flux metal reaction. The precipitation of copper in the stainless steel strip may be attributed to the following reaction.



Similar reaction must occur with silver metal. The presence of silver is reflected by the brightness of the surface but not detected to any appreciable level by the SEM analysis.

Phase diagrams reveal that copper has got complete mutual solubility for nickel, and none with chromium at 1000°C . In iron it has got limited solubility of 5%. Silver has got solubility of 3-4% only in nickel and none for chromium. Thus copper displacement reactions are favoured to occur than the silver because of lowering of the activity of copper in the stainless steel material. There is however need for an independent study

Table 6.1

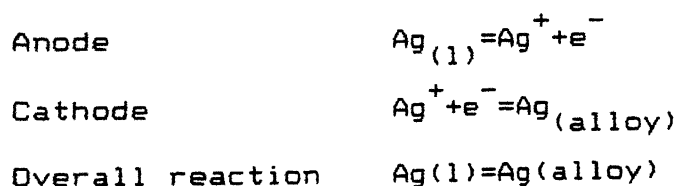
Reactions and product of concentrations

Sr. No.	Reactions	Product of concentrations at 1000°C
1)	$\text{Cu} + \text{KCl} = \text{CuCl} + \text{K}$	$(a_{\text{CuCl}} \cdot a_{\text{K}}) = 10^{-9}$
2)	$\text{Ag} + \text{KCl} = \text{AgCl} + \text{K}$	$(a_{\text{AgCl}} \cdot a_{\text{K}}) = 10^{-10}$
3)	$\text{Fe} + 2\text{KCl} = \text{FeCl}_2 + 2\text{K}$	$(a_{\text{FeCl}_2} \cdot a_{\text{K}}^2) = 10^{-22}$
4)	$\text{Cr} + 3\text{KCl} = \text{CrCl}_3 + 3\text{K}$	$(a_{\text{CrCl}_3} \cdot a_{\text{K}}^3) = 10^{-26}$
5)	$\text{Sn} + 4\text{KCl} = \text{SnCl}_4 + 4\text{K}$	$(a_{\text{SnCl}_4} \cdot a_{\text{K}}^4) = 10^{-38}$

of such reactions. For example for filler alloys containing both copper and silver, both copper and silver may go into the flux as ions. Copper may get deposited first on the substrate changing thereby the surface conditions for further spreading or depositing of silver on the already deposited copper layer. The bands found at the periphery of the droplet are analysed contain both copper and silver. Copper to silver ratio in the band is tending to decrease with an increase in the distance from the droplet. One reason for the same may be this that liquation phenomenon occurs during slow cooling of the plate in the furnace. The first solid to precipitate out is rich in copper as shown by binary phase diagram and the remaining liquid which is rich in silver may tend to spread further. Further studies may be planned to sort out the discrepancies.

It is not possible to discuss the results of cell measurements made the present study because of the complexity of the reaction and layering of the flux ingredients in the system.

The electrochemical cell made in the present work corresponds to an concentration cell as follows.



$$E = -(RT/nF) \ln a_{\text{Ag}} \quad (6.1)$$

Where a_{Ag} is the activity of silver in the metal strip, E is the e.m.f., R is the gas constant, T is the experiment temperature, and F is the Faraday's constant.

By using equation (6.1) one may show that a voltage of 0.5 volts corresponds to activity of silver in the metal strip as .01

and voltage to obtain the current, or vice versa. Similarly, one may show that if the deposition occurs by an electrochemical mechanism, the amount of current to deposit .001gm. of the silver on the strip in 30 mins. of time is must be of the order of .55mA.. A part of weight gain by deposition of silver phase may be balanced by the loss in the weight of strip due to the flux-metal reaction. Further studies may be planned to study the electrochemical behaviour of the flux reaction using single constituent fluxes.

and voltage of 0.25 to the activity of .10. Similarly one may show that if the deposition occurs by an electrochemical mechanism, the amount of current to deposit .001gm. of the silver on the strip in 30 mins. of time is must be of the order of .55mA.. A part of weight gain by deposition of silver phase may be balanced by the loss in the weight of strip due to the flux-metal reaction. Further studies may be planned to study the electrochemical behaviour of the flux reaction using single constituent fluxes.

CHAPTER SEVEN

SUMMARY AND CONCLUSIONS

Fluxes promote wetting by providing a clean metal surface. Solid metal-liquid flux interface is replaced by the solid metal-liquid filler metal interface to provide the metallurgical bond in brazing. Fluxes must dissolve the chromium oxide film on the stainless steel substrate and must protect from any atmospheric reoxidation in order to obtain good wetting on such substrates. In addition to providing clean surface, fluxes take part in number of chemical and electrochemical reactions which are important to study and understand for getting optimum results during brazing.

In the present work, the flux-metal and flux-filler metal reactions have been studied by carrying out the area of spread, weight loss, dip coating, and electrochemical cell experiments. A special silicon carbide box furnace was fabricated for the study. Both commercially available and synthetic fluxes were used. Copper-silver and copper-silver-tin alloys of various compositions were prepared. The important findings of the studies are summarised below.

- (i) The brazing flux available in the market promoted wetting by providing a clean metal surface. However, the efficiency of flux in providing a clean surface was retarded by increasing the time of contact between the flux and

solid. The area of spread and band width adjoining the spread mass tend to decrease with increased time of reaction.

(ii) In presence of stainless steel substrate and atmospheric oxygen, the flux and substrate got blackened after certain length of time. The blackening may be due to presence of excessive chromium oxide in the flux.

(iii) No blackening of strip was observed when dipped completely in the molten flux, but in partially dipped condition the part remaining above the molten flux bath but exposed to flux vapours and atmospheric oxygen rapidly corroded.

(iv) No wetting occurred when using binary mixtures of boric acid and borax. Addition of KCl either to boric acid or to the binary mixtures of boric acid-borax provided wetting and the best results were obtained with 90% boric acid, 10% KCl. Best wetting results were obtained when using pure copper filler metal, however all the alloys of binary copper and silver wet the stainless steel substrate. The flux remained stable whereas there was no blackening of the fluxes and the substrate in the flux-metal reactions.

(v) The bands or coatings were observed around the periphery of the spread mass in all the wetting experiments. Presence of KCl in the flux caused silver and copper in the filler metal to go into the flux as ions and get deposited on the substrate ahead of the droplet.

(vi) The flux-metal reactions have been given using thermodynamic and phase diagram data.

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APPENDIX A

WETTING AND SPREADING

In wetting phenomena surface energy plays a very important part. Surface tension of the liquid is not the only factor which determines whether or not solid will be wetted, but also that the tension of the interface between the solid and liquid metal exerts an almost dominant influence. Small amount of third component added to the molten or solid metal may considerably influence wetting.

An analysis of wetting and spreading is dependent upon two theories, the first is thermodynamic theory, which defines the shape which the liquid will attempt to achieve to keep its surface free energy minimum whilst the second theory is dynamic theory, which tells about a rate at which the liquid will approach this final state.

Surface Tension Theory

Calculations on the behaviour of liquid surfaces are made either by considering energy changes involved when surface layer moves, or by the concept of surface tension. The wetting of solid surface by liquid is determined by the surface tension, γ which can be derived thermodynamically from the change in the Gibbs free energy, G , of a system, when the surface area, A , is altered:

$$\gamma = \left(\frac{\partial G}{\partial A} \right)_{P,T,n}^{18}$$

for constant pressure P , Temperature T , and number of atom n ,

in the system.

In case of a liquid droplet on a flat surface three surface tensions are involved, γ_l = surface tension of liquid, γ_s = surface tension of the solid surface, γ_{ls} = interfacial tension of the liquid/solid interface.

The condition for equilibrium is minimum total free energy. Where gravitational forces are absent, the shape of the droplet is a part of sphere and

$$G_{\text{total}} = G_{\text{solid}} + G_{\text{liquid}} + G_{\text{interfacial surface}} + G_{\text{bulk}} =$$

$$\gamma_s (\text{Solid surface area}) + \gamma_l (\text{Liquid surface area})$$

$$+ \gamma_{ls} (\text{Interfacial surface area}) + \text{Shape dependent terms of the bulk.}$$

To determine the condition for equilibrium G_{total} is differentiated with respect to one of the dimensional parameters of the droplet, e.g. the height. Taking $dG/dh = 0$, for the conditions of an unchanged volume of the droplet and a flat solid surface and interface one obtains:

$$\gamma_{ls} + \gamma_l \cos \theta - \gamma_s = 0 \quad (1)$$

If the gravitation is taken into account, the shape of the liquid becomes more complicated but equation (1) is still valid because the equilibrium conditions in the neighborhood of the three phase boundary remains the same. From equation (1) it is clear that wetting, i.e., a small angle θ , is promoted by small values of γ_l and γ_{ls} in combination with a relatively large values of γ_s . Oxidised solid metal is not wetted by liquid metal because surface tensions of oxides are distinctly lower than

value for the corresponding metals.

When the liquid metal has penetrated into a vertical gap of width d between two parallel plates, the pressure drop across the liquid surface is given by

$$\Delta p = \frac{2\gamma_1 \cos \theta}{d}$$

which provides the force driving the liquid through the gap between the two plates. The equilibrium height of rise is given by

$$h_{eg} = \frac{2\gamma_1 \cos \theta}{\rho g d}$$

$$\Rightarrow h = \frac{2(\gamma_s - \gamma_{ls})}{\rho g d}$$

ρ is the density, g = gravity acceleration

Maximum height is attained if $\gamma_s - \gamma_{ls} = \gamma_l$, and from equation (1) it follows that in this case $\theta=0$. Liquid column remains at h_{max} and $d=0$ if $\gamma_s - \gamma_{ls} > \gamma_l$. Since γ_s and γ_{ls} free energies are difficult to measure, not to say impossible, in metallic systems, data can be obtained only indirectly, e.g. from equation (1) by measuring θ with metals having known values of γ_l . Methods for calculating surface tension and interfacial tension have been shown by Wassink¹⁸ from the heat of vaporization.

Effect of Addition of a Third Component and Formation of Intermetallic Wetting Component

In many cases wetting mainly occurs or is improved by the other component in the alloy. For instance, Copper is responsible for wetting of an Iron surface by Ag-Cu alloy often used in brazing.

Addition of small amount of Pd to Ag shows a marked effect

on promoting wetting of several Iron base metals¹⁹. Since Pd and Ag and also Pd and Fe, have complete mutual solubility but Ag and Fe do not, hence $E_{\text{Pd-Fe}} < E_{\text{Ag-Fe}}$ (E bond energy which is negative). On addition of Pd to Ag high energy Ag-Fe bonds on the interface can be replaced by Pd-Fe and Pd-Ag bonds, thus reducing γ_{1s} (interfacial energy) by 30%. Wetting is also improved when Pd is added to solid Fe but extent is lower than previous case because Pd has got greater mobility in liquid Ag than solid Iron²⁰.

Pd is completely soluble in the main constituent of many technically important alloys, such as Iron, Nickel, Co, Cu, etc. and due to small Pd content, erosion of base metal is negligible. These facts have led to the development of a great number of brazing alloys containing Pd.

Those systems, in which the components form intermetallic compounds, show improved wetting properties. The greater the solubility of the metals in the solid state, the lower will be the interfacial energy when these metals are brought into contact with one another. For instance, in lead-tin solder wetting is improved by the tin, which forms intermetallic compounds with Cu and with Fe. Measurements of γ_1 of the lead-tin alloys indicate that addition of lead lowers γ_1 , and γ_{1s} becomes smaller with a higher tin content so good wetting should be observed with high tin content.

CAPILLARY FLOW

If the flow of liquid occurs to fill a gap between two

closely held solid surface liquid-gas interfacial area does not change. The main driving force is the lowering of the energy of the system when the solid-gas interface is replaced by the solid-liquid interface. For the flow of liquid through horizontal solid surfaces of width W , separated by a gap d , fig.a the pressure difference between the entry point and the last point of contact may be determined as follows:

$$\Delta p = \eta (\gamma_{S/G} - \gamma_{S/L}) \frac{2W}{Wd} \quad (3)$$

$$\Delta p = \frac{2\gamma_{L/G} \cos \theta'}{d} \quad (4)$$

For above flow a balance of pressure viscous forces at any instance gives the following

$$\mu \frac{du}{dy} = \frac{\Delta p}{L} y \quad (5)$$

where μ is the viscosity of liquid, u velocity at distance y from the midpoint of the two solid surfaces and L the length of penetration at any time t .

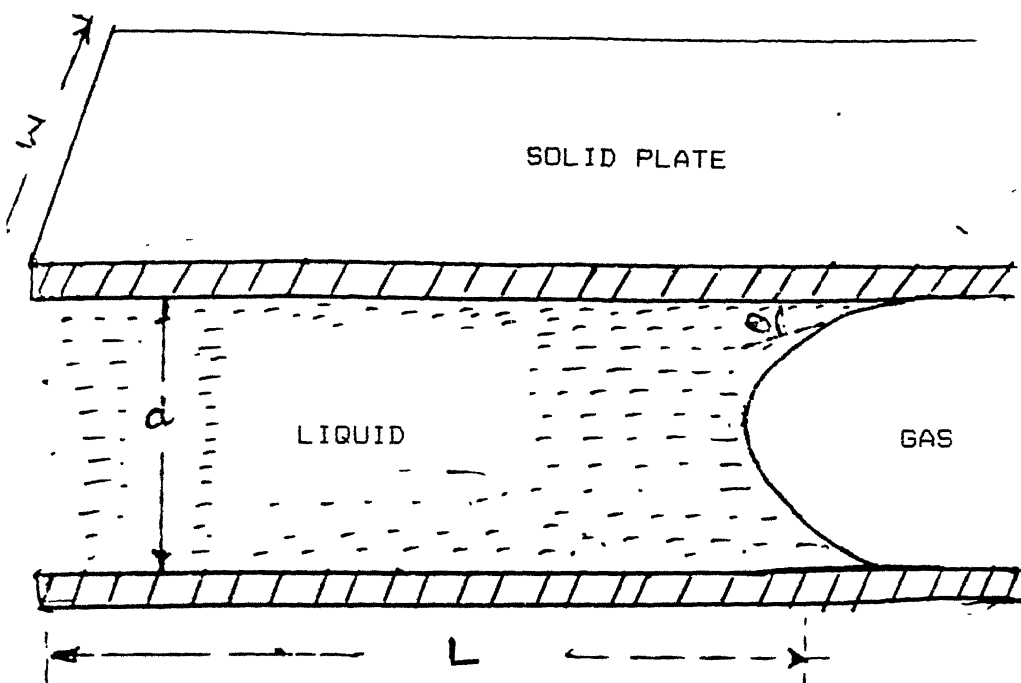
Equation (5) is solved with the boundary condition of $u=0$ at $y=\pm d/2$, to obtain the following:

$$u = \frac{\Delta p}{2\mu L} \left[(d/2)^2 - y^2 \right] \quad (6)$$

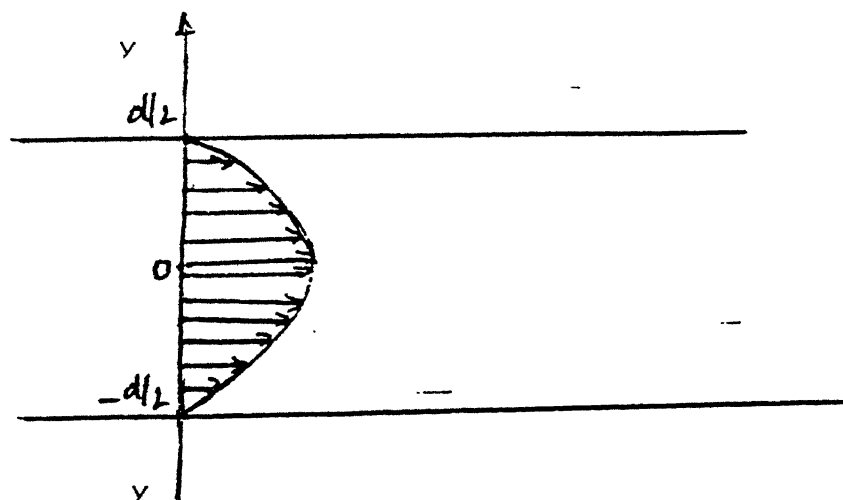
Average velocity of the liquid advancement may be determined next:

$$\bar{u} = \frac{1}{d} \int_{-d/2}^{d/2} u \, dy = \frac{\Delta p}{2\mu L} d^2 \quad (7)$$

Since average velocity gives the rate of change of the penetration with time and u can be replaced by dL/dT in equation (6),



HORIZONTAL CAPILLARY OF GAP d



VELOCITY DISTRIBUTION IN THE UNDER LAMINAR FLOW

Figure a. Liquid flow in a capillary gap between parallel plates

$$\frac{dL}{dt} = \frac{\Delta P}{2\mu L} \left[(d/2)^2 - y^2 \right] \quad (7)$$

$$\int L dL = \frac{\Delta P}{2\mu L} \left[(d/2)^2 - y^2 \right] \int dt \quad (7)$$

Integration will give time of filling of a capillary of length L as follows:

$$t = \frac{3\mu}{\gamma_{L/G} \cos \theta'} \frac{L^2}{d} \quad (8)$$

For the flow of liquid in vertical solid surfaces, opposing gravity forces are also taken into account to yield the following results:

$$t = \frac{12\mu}{\rho \gamma_{L/G}^2 d^2} \left[-\delta g d L - 2\gamma_{L/G} \cos \theta' \rho \left[1 - \frac{L}{L_{\max}} \right] \right] \quad (9)$$

L_{\max} , the maximum distance that the liquid can cover may be written as below:

$$L_{\max} = \frac{2\gamma_{L/G} \cos \theta'}{\rho g d} \quad (10)$$

The factors that favour flow of liquid to fill a capillary length may be summarised below:

- (1) High value of driving force due to surface tension i.e. $n[\gamma_{S/G} - \gamma_{S/L}]$ or $\gamma_{L/G} \cos \theta'$.
- (2) Low value of viscosity of liquid i.e. enough superheat of liquid with minimum interaction with the solid so as not to lower its fluidity.
- (3) Increased or optimum clearance or gap between the solid surfaces.
- (4) Small length of capillary
- (5) Favourable position of the capillary.

APPENDIX-B

BASE METALS

Stainless steels may be grouped into four categories (i) Austenitic non-hardenable steels (ii) Ferritic non-hardenable steels (iii) Martensitic hardenable and (iv) Precipitation hardening steels.

(i) Austenitic Non-hardenable Stainless Steels

These steels are alloy of Iron, chromium and Nickel (or Mn). The Ni or Mn additions stabilize austenite, and cause these alloys to be nonmagnetic and nonhardenable. This class of steel is the one possessing the highest heat and corrosion resistance.

A major precaution in brazing these materials is that the stabilized grades, such as type 302 and 304, are subject to carbide precipitation when held at temperatures in the range of 427° - 876°C , with a consequent loss of corrosion resistance. Carbide precipitation can be minimized by making the brazing thermal cycle as short as possible.

Carbide precipitation in stainless steel can also be eliminated by the addition of carbide stabilizing elements Ti and columbium. Low C unstabilized grades are relatively insensitive to carbide precipitation and can be brazed with essentially same range of filler metal and heating cycles as the stabilized types.

(ii) Ferritic Nonhardenable Stainless Steels

These stainless steels are basically low C alloys of Fe and Cr, where sufficient chromium has been added to Iron to stabilize ferrite. Type 430 is widely used grade that is particularly subject to a form of interface corrosion when brazed with some BAg filler metals caused by electrochemical action whereby the bond between base metal and filler metal is destroyed. It has been found that the addition of small percentages of Ni to silver base filler metals prevents interface corrosion of brazed joints in most stainless steel.

(iii) Martensitic Hardenable Stainless Steels

These are Iron-C-chromium alloys of two basic types; the low Cr, low C grades and the high Cr, high C grades. These steels are capable of being hardened by heat treatments because of their composition.

(iv) Precipitation Hardening Stainless Steels

Stainless steel have been developed for applications where high strength plus heat and corrosion resistance are required. These alloys are basically stainless steels to which alloying elements such as Al, Ti, Cu and Mo have been added to precipitation harden the alloys by special heat treatments.

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